

A Method of Ultimate Analysis of Organic Substances Developed from Combustion in a Bomb Calorimeter

EXTRACTED FROM A DISSERTATION SUBMITTED BY PETER J. MERKUS
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Methods of ultimate analysis of organic compounds by determination of the composition of the gases after combustion in a bomb calorimeter are not new. The common method has been to connect an absorption train to the bomb and bubble all the gases through it.

Watkins²¹ measured the volume of gas from the bomb in a gasometer, analyzed the gas for carbon dioxide, and determined total carbon in fuels by this method. Carr and Rente⁶ passed the gas into a rubber balloon under water and measured the amount of water displaced, after which the gas was analyzed in the usual manner. Cunningham⁷ determined sulfur in coal by burning it in a bomb in which a standard solution of barium chloride was placed which precipitated the sulfuric acid formed during the combustion. The excess of barium salt was then treated with sodium carbonate, and the barium carbonate titrated by a standard hydrochloric acid solution.

Muraour and Aunis^{15, 16} in their work on combustion of high explosives, and Bradley and Rosecrans⁴ in their work on maximum pressures during explosions, suggested that hydrogen might be found by the difference in pressure before and after the explosion, but gave no experimental data. Bosnjakovic² determined the hydrogen in this way but used a small pressure gauge to determine the initial and final pressures, which was not accurate enough to obtain satisfactory results. Since the hydrogen content is to be calculated from the difference between the initial and final pressures it is necessary to obtain a method of determining pressure which will give a fair accuracy for the absolute pressure, and the highest possible accuracy for the differential pressure. Only then can the method of Bosnjakovic be used.

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Measurement of Pressure

For the measurement of pressure up to about 600 pounds per square inch, the research worker has a very limited number of methods of observation at his command. The ordinary Bourdon gauge is too inaccurate to obtain satisfactory measurements. This gauge must be calibrated, and the variation in room temperature is enough to cause serious errors when it is used to measure a small pressure difference at high pressures. A pressure reading when approached from a lower pressure level will be slightly different from the reading of the same pressure, if it has been approached from a higher pressure level.

A mercury manometer to measure such high pressure is prohibitive due to its inconvenience. Five hundred pounds' pressure would require a mercury column of about 83 feet in height. The changes in temperature and the compressibility of the mercury throughout the column would have to be corrected for. The dead weight gauge is only satisfactory when the cylinder on which the weights are set is kept as nearly free from friction as is possible. This may be done by rotating this piston, but the cost of such equipment is quite high, while the cheaper instruments have a tendency to leak somewhat.

Kamerlingh Onnes,^{9, 10} Bridgman,⁵ Lafay,¹² and others have used the change in resistance of various metals for measurement of high pressure. For platinum, for instance, the variation of resistance with pressure may be expressed by the following equation:¹²

$$\frac{r-r'}{r} = -1.86 \times 10^{-6} P \text{ in which}$$

P = pressure in atmospheres,
 r = resistance at pressure P ,
 r' = resistance at one atm.

The temperature must be kept constant, however, because the temperature coefficient is 1900 times the pressure coefficient of resistance. Mercury is better in this respect, since the temperature coefficient is only 20 times the pressure coefficient. Manganin which is an alloy of 82% copper, 15% manganese, and 3% nickel, is now universally used in measuring high pressures by this method. These instruments, however, while

relatively accurate at very high pressures (500 atmospheres and upward) are not useful for pressures as low as 500 pounds, since the variation in resistance over a range of 500 pounds is almost negligible, and the measurement of a pressure difference of about 50 pounds would be quite impossible.

Wildhagen²² developed an instrument which consists in principle of a mercury filled differential steel manometer in one arm of which is a fine platinum resistance wire co-axial with the tube. On applying a pressure differential to the manometer the mercury rises in the arm containing the wire, and decreases the electrical resistance of a circuit of which the previously calibrated platinum wire forms the major resistance. In such an instrument errors due to the contamination of the mercury might well prove serious and fouling is difficult to avoid in practice. Were the mercury contaminated, it would adhere to the wire on receding after making an observation, and subsequent lesser differential readings would be in error owing to the change in apparent resistance of the exposed wire.

Boyd,³ in 1930, devised a manometer for the measurement of small pressure differentials at high pressures. The instrument does not require any calibration, and the use of clean mercury is not imperative. Essentially, the instrument consists of a mercury filled reservoir of relatively large diameter beneath the mercury surface of which projects the lower end of a riser of relatively small bore in which runs a movable screw rod enabling the completion of an electrical circuit through the mercury. The level of the mercury is found by moving the screw rod to make and break contact, and then the relative position of the screw rod is obtained by measuring the position of the top from a fixed reference plane by a micrometer depth gauge. In the operation of the manometer the gas is allowed to enter the instrument, and the pressure on both sides of the instrument equalized by a by-pass valve. A zero reading is then taken, the by-pass valve closed, and the upstream valve opened. When equilibrium is reached the reading on the screw rod is again taken and the difference in mercury levels calculated. This apparatus does not measure absolute pressure, and the construction does not allow a reading of differential pressure exceeding a few inches of mercury.

Washburn,²⁰ developed a method with which the pressure of a system can be measured without the use of expensive pressure measuring equipment. By filling one bomb, A, with the system under consideration, and a twin bomb, B, with a reference substance, and then adjusting the two pressures to exact equality (at a given temperature) with the aid of a pressure equalizer, the ratio PV_0/T per gram for the two systems can

be accurately determined by weighing the two bombs. No pressure measurement is involved. If now the volume of bomb B is known, the value of PV_0/T for the system under investigation can be computed to the accuracy with which PV_0/T is known for the reference substance. In this way an ordinary balance and a set of weights can be utilized as a laboratory tool for the accurate determination of high pressure. This method must also be destined for extremely high pressures, since it is difficult to obtain a balance accurate enough to read to 0.1 gram when a weight of about 3000 grams is involved.

We believe we have developed a method which will determine the absolute pressure of a system with high accuracy. Differential pressures may also be obtained with the accuracy with which a mercury manometer may be read.

Description of Apparatus

The essential parts of the apparatus are two bombs and a glass leg manometer, as shown in Figure 1. The bomb in which the explosion of the sample occurs, is a standard oxygen bomb made of illium or other acid resisting alloy. The auxiliary bomb may be made of steel and is equipped with two needle valves, so that mercury which partly fills this bomb may be withdrawn through one of them. The glass manometer is eight feet long and will show a differential pressure of 50 pounds. The glass tubing used for the manometer is pyrex glass capillary tubing. The various parts of the apparatus are connected by standard 5/16 inch copper tubing and flared tube, faced couplings.† The valves used are standard 1/4 inch Lunkenheimer, carbon steel, needle valves, packed with special high pressure packing to prevent leakage on the discharge side of the valve through the packing gland.

The apparatus is divided into two parts. The explosion system consists of the explosion bomb, the copper tubing to the oxygen tank, and the leg of the manometer on that side. The second part of the apparatus consists of the auxiliary bomb, and the copper tubing which connects this bomb to its side of the manometer. In the connection between the two systems the equalizing valve 7 is located. Any difference in pressure between the two systems may be read on the manometer when this valve is closed. Valve 2 is a blow-off valve. Valve 6 is a sampling valve, through which the gases are withdrawn from the combustion bomb after the explosion, for analysis. Valve 5 shuts the combustion bomb from the rest of its system, to prevent the high pressure wave which is caused during the explosion from being distributed through the system. The sudden shock caused by the explosion would break the glass column. Valve 10, one of the needle valves of the auxiliary bomb, allows the withdrawal of mercury from that bomb through the steel tubing connected to the top of the cover

† Fittings made by Imperial Company.

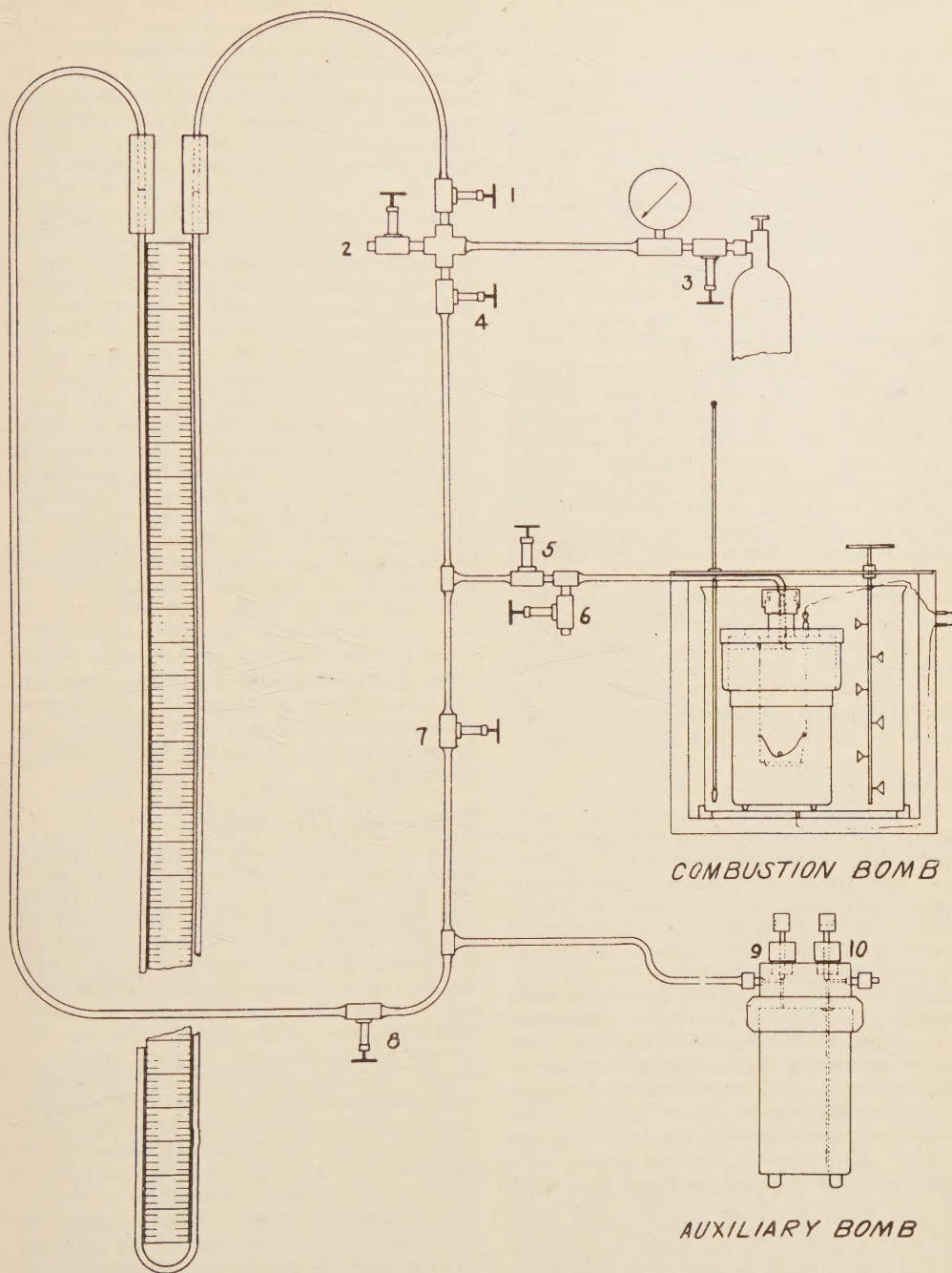


Figure 1. Apparatus for measuring pressure in a closed system

of the bomb. Valves 1, 4 and 8 merely add to the convenience of calibrating and operating the apparatus.

Calibration of the Apparatus

Since the measurement of pressure by this method depends upon the relative volumes of various parts of the system, the apparatus must be calibrated with the highest possible degree of accuracy.

The volume of the gas space above the mercury level of the manometer was calibrated by measuring the length of a weighed slug of mercury, as it was pushed along the capillary. With the aid of a plot it was possible to read at a glance the volume of gas displaced by the mercury when a change in level on the mercury column occurred.

The volume of the bombs was found by filling them with water and mercury and weighing them empty and full. The volume of the remaining parts of the system was determined by calibrating them against the mercury manometer, and by using the gas laws. A part of the system would be inflated to a certain pressure, and this pressure observed from the manometer; then the gas would be allowed to expand into the auxiliary bomb whose volume was accurately known, and the pressure read again on the manometer. The valves in all the work were opened one-half of one turn, so that there would not be any variation in the volume due to the valve stem displacement. From the data it is possible, assuming perfect gases at these low pressures, to calculate the volume of the part of the system that was tested.

Procedure

The manipulations are quite simple. A weighed amount of mercury is placed in the auxiliary bomb, and a weighed amount of the substance to be analyzed put in a pan in the combustion bomb. This bomb is set in the calorimeter jacket, and remains connected to the rest of the system at all times. The oxygen is now turned on, and after the desired pressure has been reached by the control gauge, the oxygen valve and the equalizing valves are closed. The regular calorimetric operations are now started. The rate of increase or decrease of temperature in the calorimeter is observed before the explosion, the charge fired, and the rate of increase or decrease in temperature after the combustion recorded. After all data for the heating value determination have been taken, the bomb is cooled to the temperature which prevailed before the combustion. Due to the condensation of the water of combustion in the bomb, the pressure of that system has decreased. The differential pressure of the manometer is noted. After this reading has been taken, a quantity of mercury is removed from the auxiliary bomb through the needle valve and the reading of the manometer again recorded. The amount of mercury re-

moved is weighed, and all data needed for the pressure determination will have then been taken. The gas in the bomb may now be removed for analysis. The water used in the calorimeter jacket is preferably kept at the temperature of the room so that it is unnecessary to insert the auxiliary bomb in the calorimeter jacket. The gases in the bomb after combustion consist of carbon dioxide, oxygen, and nitrogen. A sample is withdrawn and analyzed in the usual manner.

After the analysis, the remainder of the gas may be removed from the bomb, which is then washed out with boiling water. The bomb washings are titrated for total acidity with a standard sodium hydroxide solution. The sulfur after the explosion is all present as sulfur trioxide, which forms sulfuric acid on dissolving in water. The sulfur burns to sulfur dioxide, and the nitrogen present in the bomb acts as a catalyst for the oxidation of the sulfur dioxide to sulfur trioxide.¹⁹ After titration for total acidity, the sulfuric acid is precipitated with barium chloride. The amount of barium sulfate may be determined by weighing the precipitate, or by the use of a sulfur photometer. The acidity accounted for by the sulfuric acid is then subtracted from the total acidity and the remainder calculated as nitric acid formed by the oxidation of the nitrogen in the gas or the sample to nitric oxide, which formed nitric acid on solution in water.

The method of calculation will now be derived, and illustrated by a calculation. The nomenclature used is stated in Table 1. The first step is to determine the initial and final pressure of the system.

Measurement of Pressure

For the measurement of pressure the auxiliary bomb is partly filled with a weighed amount of mercury. The system is inflated with oxygen from the tank with all valves open except the blow-off valves. The pressure is measured approximately by a small oxygen gauge which acts as a control gauge. When the desired pressure is reached, the oxygen is turned off, and the equalizing valve⁷ which is located in the connection between the two separate systems, is closed. In order to obtain a convenient reading on the manometer, the blow-off valve may be opened, and a small amount of gas allowed to escape. During the regular explosion, this is automatically taken care of by the decrease in pressure in the combustion bomb due to the condensation of water vapor. When a satisfactory differential pressure is reached the blow-off valve is shut, and the pressure differential noted on the manometer. Some mercury is then allowed to flow out of the auxiliary bomb which causes a different reading on the manometer. This reading is again observed, and the mercury which was taken from the bomb is weighed.

All data have then been taken to obtain the original pressure in the system.

After the system is filled with oxygen, the pressure on both sides is P_1 . The total volume on the side of the explosion bomb is V_a and on the side of the auxiliary bomb is V_b . Explosion or blow-off decreases the pressure on the explosion side, and causes the mercury level to rise on that side. This also allows the mercury level to drop on the other side, thus increasing the volume on that side to $(V_b + \Delta V_b)$. This increase in volume is accompanied by a corresponding decrease in pressure, but since the change is small we may assume perfect gases, and take the drop in pressure as inversely proportional to the increase in volume. Thus the pressure on the auxiliary side may be assumed to be:

$$\frac{V_b}{V_b + \Delta V_b} P_1 \quad (1)$$

The differential pressure from the mercury levels is X atm. and the pressure in the combustion bomb is P_2 , so we may set up the following equation:

$$\frac{V_b}{V_b + \Delta V_b} P_1 - X = P_2 \quad (2)$$

$$\frac{V_b}{V_b + \Delta V_b} P_1 - X = \frac{V_a' + \Delta V_a'}{V_a'} P_3 + \frac{V_a' + \Delta V_a'}{V_a'} Y$$

$$P_3 = \frac{V_a' V_b P_1}{(V_b + \Delta V_b) (V_a' + \Delta V_a')} - Y - \frac{V_a'}{V_a' + \Delta V_a'} X$$

Some mercury is now removed from the auxiliary bomb which causes the mercury levels in the manometer to change, and the volume of the gas in the auxiliary increases by the volume of mercury that has been removed, but decreases by the volume which is taken up by the rising mercury column on that side of the manometer. On the other hand the explosion side of the system increases in volume due to the drop in mercury level. Therefore, the pressure in bomb A will change from P_2 to

$$\frac{V_a'}{V_a' + \Delta V_a'} P_2 \quad (3)$$

The pressure in the auxiliary bomb is now P_3 , and the differential pressure by mercury levels is Y . We can then set up the following equation:

$$\frac{V_a'}{V_a' + \Delta V_a'} P_2 + Y = P_3 \quad (4)$$

Y is always positive if the pressure on the auxiliary side is larger than on the explosion side throughout the test, but becomes negative as soon as the pressure on the explosion side exceeds that on the auxiliary side after mercury withdrawal.

If the auxiliary bomb is now considered as a separate system, the initial conditions were P_1

for the pressure, and V_b for the volume; the final conditions were defined as P_3 for the pressure, and V_b' for the volume. For condition (1) we may say

$$P_1 V_b = \rho_1 n R T \quad (5)$$

and for condition (2)

$$P_3 V_b' = \rho_3 n R T \quad (6)$$

But since R is a constant, and n the number of mols of gas and the temperature T were kept constant throughout the duration of the run, we may state

$$P_1 V_b / \rho_1 = P_3 V_b' / \rho_3 \quad (7)$$

or

$$\rho_3 P_1 V_b = \rho_1 P_3 V_b' \quad (8)$$

We can now, with the aid of equations (2) and (4) get P_3 in terms of P_1 , and then equation (8) may be solved for its only unknown P_1 . After this value has been found, P_2 , the pressure after the explosion, can be solved for directly by the aid of equation (2). Solving both equations (2) and (4) for P_2 we obtain:

$$P_2 = \frac{(V_a' + \Delta V_a')}{V_a'} P_3 + \frac{(V_a' + \Delta V_a')}{V_a'} Y \quad (9)$$

Equating (2) and (9) and solving for P_3 ,

Substituting the value of P_3 in equation (8), and solving for P_1 , we get:

$$P_1 = \frac{-\rho_1 V_b' Y - \frac{\rho_1 V_b' V_a' X}{V_a' + \Delta V_a'}}{\rho_3 V_b - \frac{\rho_1 V_b' V_a' V_b}{(V_b + \Delta V_b) (V_a' + \Delta V_a')}} \quad (10)$$

In this equation P_1 is the only unknown; all other factors are determined during the experimental work or are constants.

The accuracy with which the absolute pressure may be determined depends upon the accuracy with which the volume of the individual parts of the system is known.

The auxiliary bomb was used as a primary standard, because it was equipped with two needle valves, and its volume was measured numerous times, so that this was known to about 0.1 cc. This is an error of only 0.03%. The volume of the other parts of the apparatus which were calibrated by using this bomb and the mercury manometer, is therefore known to that accuracy. The accuracy with which the hydrogen content may be determined depends upon the accuracy with which the differential pressure can be observed. This, however, is obtained from the difference in mercury levels of the manometer which can be read to 0.5 mm.

A correction must be made for an error in the analysis of the combustion gases. The gases as they flow from the bomb are saturated with water vapor. For instance, at 26° C., the vapor pressure of water is about 25 mm. Assuming the total atmospheric pressure to be 750 mm. then the volume of the water vapor in 100 cc. of gas will be $25/750 \times 100$ or 3.33 cc. When the carbon dioxide is absorbed, a proportional amount of water vapor disappears with it, so in order to obtain the net amount of carbon dioxide in the gas this amount of water vapor must be subtracted. A similar correction must also be made in the case of the oxygen and nitrogen.

Mathematical Considerations

In order to convert the data into the desired results the following equations formulated by Mollier¹⁴ and Ostwald^{17, 18} may be used. The nomenclature is shown in Table II.

Assuming that the substance contains no water,

$$c + h + o + n + s + a = 1.00 \quad (11)$$

Using the fuel characteristic formula:

$$\delta = 1 + 3 \frac{h - \frac{o - s}{8}}{c} \quad (12)$$

This equation has been modified for our purpose because in an oxygen bomb the sulfur upon combination, is converted to SO₃ instead of SO₂. If N₂ is present as a catalyst the conversion to SO₃ is complete as has been shown by Regester.¹⁹ The fuel characteristic formula then reads as follows:

$$\delta = 1 + 3 \frac{h - \frac{o - 1.5s}{8}}{c} \quad (13)$$

For the carbon content the equation is as follows:

$$\rho = \frac{12P_2VaCO_2}{\rho_2\beta RT} \quad (14)$$

TABLE I

NOMENCLATURE USED IN EQUATIONS 1-10

Explosion bomb	
Va	volume of combustion system before explosion in cc.
Va'	volume of combustion system after explosion.
$\Delta Va'$	increase in volume of the "A" side system due to fall in mercury level on "A" side because of mercury withdrawal on the "B" side.
Auxiliary bomb	
Vb	volume of gas space of "B" side system before mercury withdrawal and before the explosion.
ΔVb	increase in volume of "B" side system due to drop in mercury level on "B" side, because of explosion on "A" side.

Vb'	volume of gas space of "B" side system after mercury withdrawal.
P ₁	original pressure of the system in atmospheres absolute.
P ₂	pressure in bomb "A" after combustion.
P ₃	pressure in bomb "B" after mercury withdrawal.
X	differential pressure on manometer after explosion, in atm.
Y	differential pressure on manometer after mercury withdrawal.
$\rho_1\rho_3$	gas law deviation constants corresponding to pressure P ₁ and P ₃ .
R = 82.07	cc. atm. per °K per mol = universal gas constant.

TABLE II

NOMENCLATURE USED IN EQUATIONS 11-21

c, h, o, n, s, a	= weight of carbon, hydrogen, oxygen, nitrogen, sulfur and ash in sample on basis of 1 gram.
O ₂ 'N ₂ '	= mol fraction of component in the gas before the combustion.
O ₂ , N ₂ , CO ₂	= mol fraction of component in gas after combustion.
β	= weight of sample in grams.
Va	= volume of explosion bomb in cc.
P ₁	= pressure of system before explosion in atm. abs.
P ₂	= pressure of system after explosion in atm. abs.
R	= universal gas constant, 82.07 cc. atm./mol. °K.
$\rho_1\rho_2$	= gas law deviation factors corresponding to P ₁ and P ₂ respectively.
T	= temperature of system during experiment.
HNO ₃	= mols of nitric acid found by titration of the bomb washings.
δ	= fuel characteristic.
fe	= weight of ignition wire.
v	= nitrogen number of fuel = the ratio of weight per cents of nitrogen to carbon.

For the nitrogen content this equation may be used:

$$n = \frac{28Va}{R\beta T} \left(\frac{P_2N_2}{\rho_2} - \frac{P_1N_2'}{\rho_1} \right) + \frac{14HNO_3}{\beta} \quad (15)$$

The available hydrogen which is the H left in the substance after the oxygen present in the substance has been combined with the H to form H₂O, may be calculated from the following equation:

$$h' = \frac{c}{3} (\delta - 1) - \frac{3S}{16} \quad (16)$$

in which

$$\delta = \frac{\frac{P_1 \rho_2}{P_2 \rho_1} - 1}{\frac{P_2 \rho_1}{CO_2} + v + 1} - \frac{9/56 Fe + 21 HNO_3}{\beta c} \quad (17)$$

in which

$$v = \frac{N_2 - \frac{P_1 \rho_2}{P_2 \rho_1} N_2^1}{CO_2} + \frac{6 HNO_3}{\beta c} \quad (18)$$

The total hydrogen may be found by the use of the formula:

$$h = \frac{8/3 c (\delta - 1) + 1 - (C + n + a + 2.5s)}{9} \quad (19)$$

The sulfur is found by analytical methods from the bomb washings after the combustion of the material. The oxygen may be found by difference. In the case of the analysis of petroleum products, equation (17) may be somewhat simplified. The value of v will be about 0.01 for all petroleum fractions and the value of the term $-\frac{9/56 fe + 21 HNO_3}{\beta c}$

will be about -0.01 , so these terms cancel. The resulting equation will then read as follows:

$$\delta - 1 = \frac{\frac{P_1 \rho_2}{P_2 \rho_1} - 1}{CO_2} \quad (20)$$

and then

$$h' = \frac{4Va}{\beta RT} \left(\frac{P_1}{\rho_1} - \frac{P_2}{\rho_2} \right) - \frac{3s}{16} \quad (21)$$

The Deviation of Mixtures of Oxygen and Carbon Dioxide from the Perfect Gas Laws

Mixtures of carbon dioxide and oxygen deviate from the gas laws quite decidedly. A mixture of 30% of carbon dioxide and 70% oxygen at 20 atmospheres deviates to the extent of 4%. Since such errors cannot be allowed in the ultimate analysis by the method that has been described in the foregoing pages, these deviations had to be taken into consideration.

Even though both oxygen and carbon dioxide have been thoroughly investigated by Amagat,¹ and Kamerlingh Onnes,^{8, 9, 10} as to the deviations from the gas laws, mixtures of these two gases have not been experimented with to any great extent. Keesom¹¹ has investigated mixtures of oxygen and carbon dioxide, but of carbon dioxide content of over 80%, and at pressures over 60 atmospheres. Bosnjakovic² has determined the deviations for mixtures of lower carbon dioxide content, and at lower pressures.

Data from the International Critical Tables,⁸ from Kamerlingh Onnes,^{8, 9, 10} Landolt Börnstein Tabellen¹² and Bosnjakovic² have been recalculated to obtain the gas law deviations for mixtures of oxygen and carbon dioxide for the range

of pressures and carbon dioxide concentrations used in this work.

The values for ρ , the deviation factor, were plotted against the carbon dioxide content at any pressure at two temperatures, so that the deviation for any mixture of carbon dioxide and oxygen at any pressure could be read from the graph. The correction for temperature was made by interpolation between the two temperatures plotted, 18° and 24° C.

Kamerlingh Onnes^{8, 10} suggests the following empirical formula to be used for gas mixtures of carbon dioxide and oxygen, with a carbon dioxide content below 30%.

$$\rho = \rho_{CO_2} PT_{CO_2} CO_2 / CO_2 T \quad (22)$$

For gas mixtures containing over 30% of carbon dioxide the following formula should be used:

$$\rho = \rho_{O_2} PT_{O_2} / P_{O_2} T \quad (23)$$

From the International Critical Tables we may obtain the PVT relations for pure oxygen, which are expressed by the equations:

$$\text{At } 0^\circ \text{C.} \\ pv = 1.001 - 0.000994 p + 0.00000219 p^2$$

$$\text{At } 20^\circ \text{C.} \\ pv = 1.07425 - 0.000753 p + 0.0000015 p^2$$

$$\text{At } 50^\circ \text{C.} \\ pv = 1.1842 - 0.000491 p + 0.0000017 p^2$$

These equations were plotted so that it was possible to obtain the value of "pv" at any pressure and any temperature. The temperature curves were obtained by interpolation. The data from Bosnjakovic was then recalculated and plotted so that it was possible to read off the gas law deviation of any gas mixture of carbon dioxide, and oxygen, at any pressure, and any temperature.

Figure 2 shows the deviation of oxygen-carbon dioxide mixtures at any pressure at 18° C.

Figure 3 shows these deviations at 30° C. The factors for temperatures between 18-30° C. are obtained by interpolation.

Example of Calculations

An example will more clearly demonstrate the use of the method. The following example shows the calculations of the data obtained in the analysis of a sample of thio-urea.

Data Taken in Analysis of Thio-Urea

$\beta = 0.6250$ grams	
Volume of mercury placed in auxiliary bomb	
	= 143.30 c.c.
Volume of mercury removed	= 32.55 c.c.
Manometer Readings	
After explosion:	
A = 153.00 c.m.	(5.38 c.c.)
B = 94.20 c.m.	(10.98)

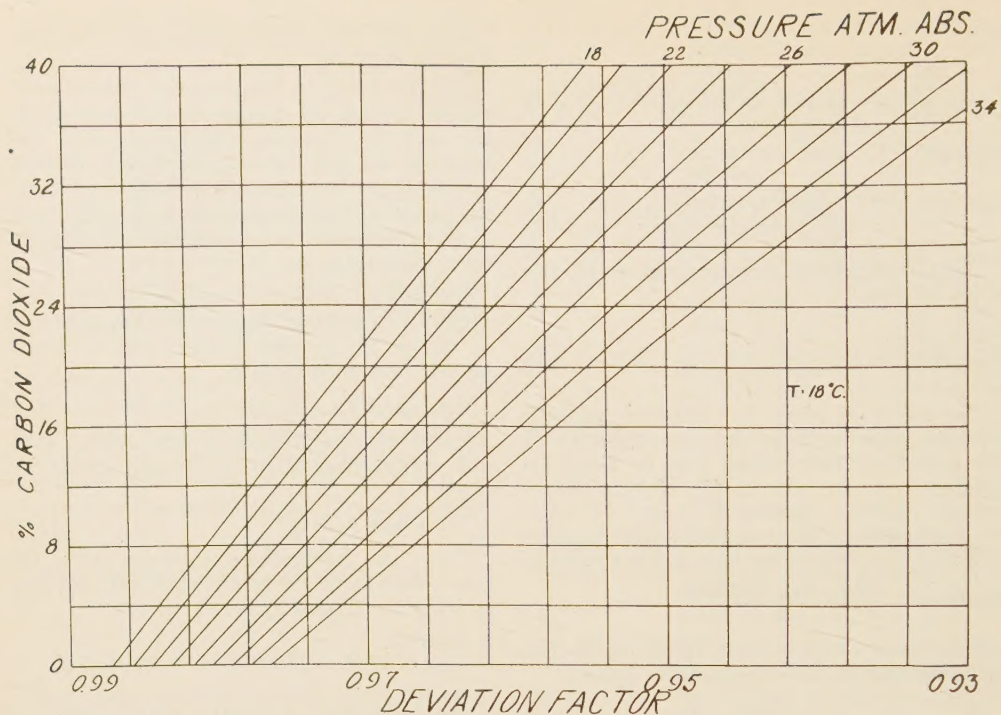


Figure 2. Deviation of oxygen-carbon dioxide mixtures at any pressure at 18° C.

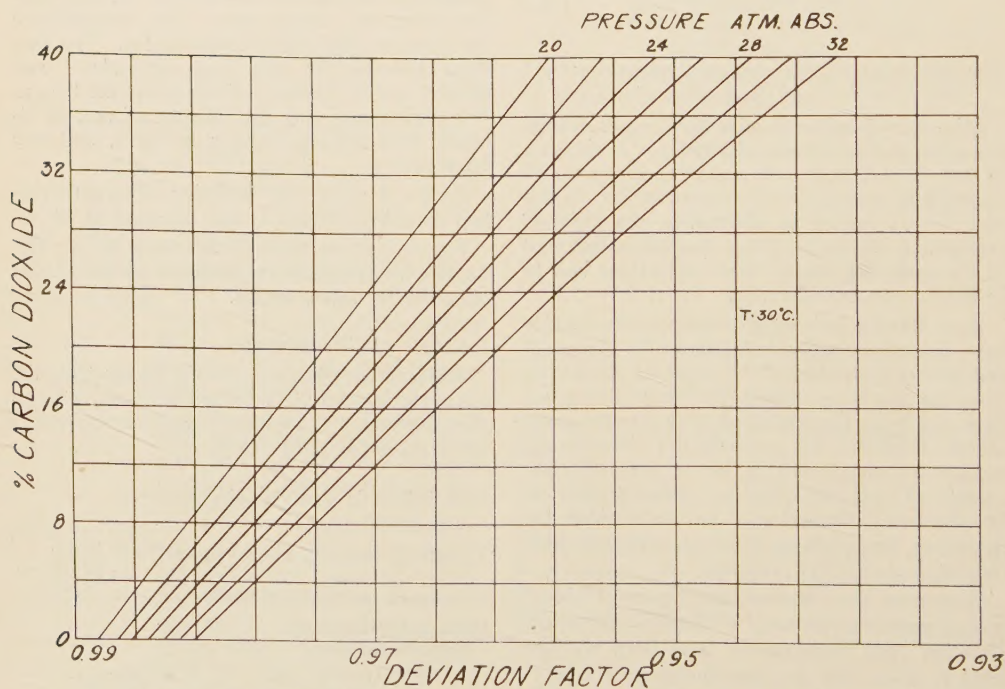


Figure 3. Deviation of oxygen-carbon dioxide mixtures at any pressure at 30° C.

After mercury removal:

A = 74.60 c.m. (9.79 c.c.)
 B = 151.00 c.m. (6.57 c.c.)

Composition of gas before explosion:

O₂ = 97.16%
 N₂ = 2.84% (calculated)

Composition of gas after explosion:

CO₂ = 1.80%
 O₂ = 93.46%
 N₂ = 4.34% (by difference)

Bomb washing titration 205.43 c.c. n/10 NaOH

Weight of barium sulfate = 1.9084 grams

Temperature throughout run = 296.6° K.

Calculations of the composition of Thio-Urea:

From the control gauge we find that the initial pressure was about 300 lbs., and the final pressure about 290 lbs. From these data we may obtain the values for ρ_1 and ρ_3 .

$$\rho_1 = 0.9867 \quad \rho_3 = 0.9833$$

Also we find that:

$$\begin{aligned} X &= 58.80 \text{ c.m.} & Y &= -76.40 \text{ c.m.} \\ Vb &= 421.81 - 143.30 = 278.51 \text{ c.c.} \\ \Delta Vb &= 1.95 \text{ c.c.} \\ Vb' &= 421.81 - 110.75 - 2.46 = 308.60 \text{ c.c.} \\ Va' &= 553.64 - 1.95 = 551.69 \text{ c.c.} \\ \Delta Va' &= 1.95 + 2.46 = 4.41 \text{ c.c.} \end{aligned}$$

Substituting these values in the equations for

P_1 (10), we obtain

$$\begin{aligned} P_1 &= 1570.6 \text{ c.m.} \\ P_1 &= 303.7 \text{ lbs./in}^2 \end{aligned}$$

The value for P_2 is obtained by substitution in equation (2)

$$P_2 = 290.3 \text{ lbs./in}^2$$

Carbon: Substituting the data in equation (14) for the carbon content:

$$C = 0.1579 \text{ or } \% \text{ Carbon} = 15.79$$

Sulfur: Weight of barium sulfate = 1.9084 grams corresponding to .2621 grams of sulfur

$$\% \text{ S} = .2621/.6250 = 41.94$$

Nitrogen: 0.2621 grams of sulfur = 0.80275 grams H₂SO₄

$$= 164.36 \text{ c.c. N/10 NaOH}$$

Acidity of HNO₃ = 205.43 — 164.36 = 41.07 c.c.
 = 0.004107 Mols HNO₃

Substituting the data in equation (22) for n ;

$$n = 0.3740 \text{ or } \% \text{ Nitrogen} = 37.40$$

Hydrogen: The value for δ is obtained from equation (33)

$$\delta - 1 = 2.5067$$

$$h' = 0.1579/3 (2.5067) - (3) (0.4194)/16$$

$$h' = 0.0533 \text{ or } \% \text{ Hydrogen (available)} = 5.33$$

Percentage Composition of Thio-Urea

	<i>Determined</i>	<i>Theoretical</i>
Carbon	15.79%	15.76%
Nitrogen	37.40	36.80
Hydrogen	5.33	5.30
Sulfur	41.94	42.4
Total	100.46%	100.00%

Accuracy of Method

The accuracy of the method was checked on a number of pure substances. The results on benzoic acid, salicylic acid, sucrose, thio-urea, naphthalene and camphor are given in Table III. In this table the available hydrogen has been reported instead of the total hydrogen since the available hydrogen was the factor desired in valuing the carburetting value of gas oils, which was the immediate end in view when this method was developed. The total hydrogen and total oxygen could have been calculated equally well. The accuracy of the determinations may be seen from the table. The available hydrogen in sucrose should be zero and in five analyses the variation was only from —0.020 to +0.003%. In six complete analyses of thio-urea the maximum and mean variations from the theoretical composition were:—

	<i>Maximum Variations</i>	<i>Mean Variation</i>
C	—0.17 to +0.11	—0.05
H	—0.10 to +0.23	—0.09
S	—0.25 to +0.17	—0.02
N	—0.69 to +0.59	+0.06

The apparatus and the method of analysis could be simplified and the time of calculation shortened if a thoroughly accurate pressure gauge of the Bourdon type was available. It is believed that sufficient accuracy for commercial purposes may be obtained in a simplified system using a good commercial pressure gauge and a mercury differential manometer. An apparatus of this type is being constructed and will soon be ready for test.

Summary

Methods of determining the ultimate composition of organic compounds by analysis of the total products of combustion in a bomb calorimeter are old. It has also been recognized that if a pressure gauge of absolute accuracy was available it would be possible to calculate ultimate analyses from the drop in pressure, the analysis of a representative sample of the gas and the titration of the bomb washings. The difficulty has been that there was no method of adequate accuracy for measuring pressures in the range of a few hundred pounds per square inch. The method presented here uses a second bomb as a reference pressure vessel and determines the change in pressure after explosion by means of a differential manometer. The reference bomb is partly filled with mercury and by withdrawing

TABLE III
Analyses of Pure Materials

Substance	Carbon		Available Hydrogen		Sulphur		Nitrogen	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Benzoic Acid C_6H_5COOH	68.82	68.79 68.87 68.70 68.89 68.80	1.65	1.61 1.64 1.63 1.68 1.60				
Av.		68.81		1.63				
Naphthalene $C_{10}H_8$	93.70	93.75 92.95 93.60	6.30	6.38 6.15 6.23				
Av.		93.43		6.26				
Sucrose $C_{12}H_{22}O_{11}$	42.08	42.15 42.00 42.17 42.19 42.27	0.0	0.003 —0.015 —0.020 0.010 0.000				
Av.		52.16						
Salicylic Acid $C_6H_4OHCOOH$	60.85 61.04 61.00 60.48 61.08	60.89	0.0	0.01 —0.02 —0.008 0.08 —0.05				
Av.	60.90							
Thio-urea $CS(NH_2)_2$	15.77	15.60 15.88 15.79 15.64 15.58 15.83	5.30	5.37 5.20 5.43 5.47 5.51 5.53	42.13	42.28 42.00 41.94 41.88 42.30 42.26	36.80	36.11 37.29 37.39 37.18 36.64 36.54
Av.		15.72		5.39	42.11		38.86	
Camphor $C_{10}H_{16}O$	78.88	78.37 78.54 78.80	9.28	9.04 8.98 9.08				
Av.		78.57		9.03				

a known volume of mercury and determining the change in pressure by the differential manometer it is possible to calculate the total pressure in the calorimetric bomb before and after combustion with an error only as great as that involved in the determination of the volume of the various parts of the system and in reading the differential manometer and in making the corrections for the deviations from the behavior of perfect gases. Methods for correcting for these deviations are included in the paper. The gases from the bomb are analyzed for carbon dioxide and the bomb

washings titrated for nitric and sulfuric acids as is customary. A complete ultimate analysis of the raw material may be obtained from these data by proper calculation and it is believed that the method is more accurate and more rapid than methods ordinarily employed. The total time required for the analysis and calculations need not exceed three and one-half hours.

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